

# General Molecular Mechanics Approach to Transition Metal Complexes

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**ABSTRACT:** Transition metal complexes have been treated by a molecular mechanics approach using an MM2-like valence force field for the ligands and a Urey–Bradley force field about the metal. Metal–ligand atom bonds are parameterized with dependence on the metal covalent radius. The current metal–ligand distances and covalent radii were determined by a Simplex minimization and visual optimization of the deviations in bond distance between 230 structures from the Cambridge Crystallographic Structure Database and the force field calculated values. Moderately good reproducibility of structures is obtained with a variety of metal types with different oxidation states, and degree of unsaturation and with square-planar compounds. The current model also includes coordination of  $\pi$  ligands to the metal center with a  $1/r^6$  attractive term whose minimum is 25 kcal/mol per  $p$  orbital at a distance dependent on the covalent radius of the metal and an angular attenuation factor. © 1998 John Wiley & Sons, Inc. *J Comput Chem* 19: 1167–1178, 1998

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## Introduction

Successful modeling of organometallic species by molecular mechanics is a substantial challenge. Previous work dates back to 1959 to an attempt by Corey and Bailer to model  $\text{Co-en}_3^{3+}$  complexes, and efforts continue.<sup>1</sup> Lauher, Raber,

and Hay used a Urey–Bradley force field about the metal (no 1,3- angular potentials only atom–atom potentials) to obtain geometries at the metal,<sup>1i,j,n</sup> whereas others have used specific angular functions. In every case, a limited set of compound types (either specific metals or specific ligands) was addressed. More recent approaches use the valence state force field (1,3- interactions represented as angular potentials) with extensive parameterization to reproduce specific geometries. Furthermore, Landis has developed angular potential functions that reproduce geometries of higher coordinated metals.<sup>1l,m</sup>

Dedicated to N. L. Allinger for his insights and determination.

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Our concern has been for a more general force field that might be universally applicable, not necessarily to reproduce all molecules, but to provide a steric-electrostatic model reminiscent of VSEPR. With the success of the valence force field MM2 in modeling organic systems<sup>2</sup> and the development of the MMX force field,<sup>3</sup> which includes an aromatic carbon type, stronger out-of-plane bending constants at  $sp^2$  carbon, weaker bending constants for  $sp$  carbon, and point charges derived from bond dipole moments to calculate electrostatic interactions, we sought to model transition metal systems *in general* with a limited number of assumptions. The original model was described briefly previously<sup>3</sup> but was not evaluated with a large collection of structures. The focus of this study is a detailed description of the original model, the evolution of the parameters and potential functions in the current model, and the evaluation of the current model on both a large data set and on molecules treated by more recent attempts to apply molecular mechanics to organometallic compounds.

## Description of Original and Current Models

In the original model,<sup>3</sup> metal-ligand bond lengths are determined only by the ligand and the covalent radius of the metal, independent of oxidation state of the metal and charge on the complex; metal-ligand force constants were set equal to 2.0 mdyne/Å except with terminal carbonyls (4.0 mdyne/Å). Terminal carbonyls were originally composed of acetylenic-type (type 4) carbons and a trivalent  $O^+$  atom type (46), which have no bond dipole moment, nor any charge on the oxygen for purposes of the metal calculations. See Tables I and II for the general metal-ligand constants and the metal covalent radii, respectively.

The current model has optimized covalent radii and metal-ligand bond lengths with new atom types for terminal carbonyl carbon (type 63), carbenes (type 61), and carbynes (type 62). The force constants remain the same except that the metal-phosphine stretching force constant has been set to 1.5 mdynes/Å. See Tables III and IV for the constants and radii.

In the original model,<sup>3</sup> the geometry at the metal for penta- and higher ligated metals was determined exclusively by the ligand-ligand interaction so the bending force constant is set to 0, and

the 1,3-van der Waals interaction, which is not invoked in the valence force field of MM2 and MMX, is "turned on," using exactly the same radii, eps, and potential function for 1,4- and higher nonbonded interactions. For tetra-, tri-, and dicoordinated metals, the valence force field is still employed where bond angles are set to 109.5°, 120°, and 180°, respectively, and the bending force constant is set to a value of only 0.1 mdyne/degree, a value only one fourth that of saturated carbon bending force constants.

In the original<sup>3</sup> and current model, all other angles and torsions were determined by the MMX valence force field where the metal as a terminal atom is treated as any wild-card atom in the force field, so the angle and torsion are determined by the internal atoms and the organic terminus.

In the original model,<sup>3</sup>  $\pi$ -coordinated ligands are bonded with a  $1/r^2$  attractive potential counterbalanced by an exponential repulsive potential, which resulted in a well depth of 15 kcal/mol per  $p$  orbital at a distance determined by the covalent radius. The potential was modified by a  $p$  orbital off-axis angular attenuation factor of  $1 - (1 - \cos)^2$ .

In the current model, the attractive potential is a  $1/r^6$  term with bigger eps and a larger repulsive potential, which leads to a well depth of roughly 25 kcal/mol. Thus, the "nonbonded" coordination potential for  $sp^2$  and  $sp$   $\pi$  ligands is:

$$E_{\text{coord}} = \text{eps}(80 * 290,000 * \exp\{-12.5/p\} - 110 * (1 - (1 - \cos)^2) * p^6)$$

where eps (hardness factor) = 0.5;  $p$  = (covalent radius of the metal + 0.66)/distance of metal to the  $\pi$  atom. In the current model, the out-of-plane bending constant is set equal to zero for any trigonal atom coordinated to a metal.

For any metal not coordinately saturated, 0.15 Å is added to the covalent radius of the metal, and the 110 kcal/mol  $\pi$  attractive potential is reduced to 85% of its standard value. Also, rather than doing a VESCF  $\pi$  calculation on coordinated cyclopentadienes and simple aromatics, the aromatic carbon type is used. Bonds between aromatic carbons are 1.40 Å with a force constant of 7.5 mdynes/Å and have a total twofold torsional barrier of 60 kcal/mol.

In the original<sup>3</sup> and current model, metal-metal lengths are determined by the covalent radii and, for every additional unit increase in bond order, 0.19 Å was subtracted from the single bond value.

**TABLE I.**  
**File of Added Constants for Metal–Ligand Interactions—Original Model in MM2 Format.**

0,29,1,17 , , , , , , , , , , , , , !0 tor, 29 dist, 1 vdw, 17 angles									
6,10,2.0,1.1837 , , , , , ! type 1, type 2, kstr., r1-2, r', bmom, ss, ts									
7,12,1.0,1.35									
3,25,1. ,1.8664									
15,25,2.0,1.996									
10,41,0.5,.09534									
12,42,1.5,1.288									
1,80,2.0,2.021 , , , , , ! sp3C—metal									
2,80,2.0,1.99 , , , , , ! sp2C—metal									
3,80,2.0,2. , , , , , ! carbonyl sp2C—metal									
4,80,4.0,1.83 , , , , , ! sp C—metal									
5,80,3.0,1.50 , , , , , ! terminal H—metal									
6,80,2.0,1.80 , , , , , ! sp3 oxygen—metal									
7,80,2.0,1.60 , , , , , ! sp2 oxygen—metal									
8,80,2.0,1.98 , , , , , ! sp3N—metal									
9,80,2.0,1.91 , , , , , ! sp2N—metal amide type									
10,80,4.5,1.65 , , , , , ! sp N—metal									
12,80,2.0,2.30 , , , , , ! Cl—metal									
13,80,2.0,2.55 , , , , , ! Br—metal									
14,80,2.0,2.67 , , , , , ! I—metal									
15,80,2.0,2.30 , , , , , ! sp3 sulfur—metal									
22,80,2.0,2.05 , , , , , ! cyclopropyl C—metal									
25,80,1.5,2.28 , , , , , ! phosphorus—metal									
32,80,2.0,2.538									
34,80,2.0,2.568									
37,80,2.0,2.00 , , , , , ! sp2N—metal imine type									
38,80,2.0,2.33 , , , , , ! thion S—metal									
40,80,2.0,1.99 , , , , , ! aromatic C—metal									
45,80,2.0,1.60 , , , , , ! bridging H—metal									
46,80,3.0,1.70 , , , , , ! oxonium—metal									
33,.044, 1.94 !									
3 80 5 80 0. ,1. ,0 ! ang type, 1–2–3 types, kbnd, ang0, ang10									
4 3 7 80 0. ,1. ,0									
0 0 10 6 1. ,120.,0									
0 7 12 7 1. ,109.,0									
0 7 12 42 1. ,109.,0									
0 0 26 00 0. ,1.0 ,0									
3 0 26 0 0. ,1. ,0									
4 0 26 0 0. ,1. ,0									
0 0 32 0 .5 ,115.,0									
0 0 34 0 .5 ,109.,0									
0 2 37 80 .5 ,120.,0									
3 2 37 80 .5 ,60. ,0									
4 2 37 80 .5 ,85. ,0									
0 2 38 80 .5 ,120.,0									
0 3 38 80 .5 ,85. ,0									
3 3 38 80 .5,120. ,0									
4 3 38 80 .5, 60. ,0									

Initially, metal–ligand covalent radii were chosen from a list provided in an undergraduate text, and iron–ligand distances were accumulated from various sources, particularly Lukehart's book.<sup>4</sup> However, it became clear that coordinately satu-

rated compounds were reasonably well reproduced, but coordinately unsaturated metals had to be treated as special cases. Thus, for low-spin coordinately unsaturated metals, including square-planar systems, the metal–ligand bond length to

TABLE II.  
Covalent Radii Original Model.

Metal	Radius
Li	1.510
Na	1.85
K	2.30
Rb	2.44
Be	0.00
Mg	1.60
Ca	2.00
Sr	2.15
Sc	1.60
Y	1.85
La	1.85
Ti	1.455
Zr	1.60
Hf	1.60
V	1.355
Nb	1.455
Ta	1.455
Cr	1.26
Mo	1.39
W	1.39
Mn	1.26
Tc	1.355
Re	1.355
Fe	1.26
Ru	1.355
Os	1.355
Co	1.26
Rh	1.355
Ir	1.355
Ni	1.26
Pd	1.355
Pt	1.39
Cu	1.26
Ag	1.455
Au	1.455
Zn	1.355
Cd	1.51
Hg	1.51

unsaturated carbon is decreased by 0.15 Å; that to a halogen is decreased by 0.20 Å; and that to either an ether oxygen or sulfur is decreased by 0.1 Å. In all cases, the force constant is increased by 50%. For metals with more than 18 electrons, all metal–ligand bond distances are increased by 0.15 Å. For square-planar complexes with a chlorine or bromine trans to a carbon, hydrogen, or phosphorus ligand, the metal–halogen distance is increased by 0.2 Å and the trans ligand distance is decreased by 0.1 Å; this is the trans effect docu-

mented in many sources, Lukehart’s text among them.<sup>4</sup> Furthermore, it became important to increase the natural angle at metal-bonded phosphorus and thioether sulfur to 109.5° from the <100° values for these atoms when not bonded to a metal. Likewise, the natural angle between lone pairs on a metal-bonded oxygen is set equal to 90° so that the metal–oxygen–X angle at the oxygen of a metal alkoxide would not be constrained to a small angle.

In the current model, the changes in equilibrium distances in response to unsaturation, spin, square-planar requirements, and >18 electron metals are retained.

Results

EVALUATION

It was of particular concern to evaluate the initial parameters, to provide a systematic means of altering them, and to examine those ligands and metals that could not be adequately treated to determine the origin of the deviations, thereby to provide more atom types and still remain in the spirit of the original minimal assumption model. Thus, 233 structures from the Cambridge Crystallographic Structure Database (CSD)<sup>5</sup> were chosen for testing the model (see Table A-I in Appendix). This allowed formulation of the current model and parameters.

Compounds were chosen from the CSD on the following bases: (1) only three different types of metals could coexist in a single compound due to no-longer-existent constraints of the original MMX program; (2) no more than nine metal atoms could be present in a single compound due, again, to the original constraints; (3) the total number of atoms could be no more than 250, again due to the original constraints; (4) compounds were removed if heavy atoms were disordered, particularly if the disordered atoms were close to the metal centers; (5) compounds were removed from consideration if there were missing constants for the ligand portion; and (6) no new ligand constants were created for these compounds.

The final list of compounds contained 230 structures with significant populations of chromium, nickel, cobalt, molybdenum, iron, ruthenium, titanium, and tungsten; lesser populations of palladium, platinum, and zirconium were present (see Table V). The structures were read in directly and edited with PCModel<sup>6</sup> when atoms were incor-

**TABLE III.**  
**File of Added Constants for Metal–Ligand Interactions—Current Model in MM2 Format.**

[illegible]

**TABLE III.**  
(Continued)

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0	0	4	33	.4 ,180.,0 ! ang type, 1-2-3 types, kbnd, ang0, ang1
3	80	5	80	0. ,1. ,0
4	3	7	80	0. ,1. ,0
0	0	10	6	1. ,120.,0
0	7	12	7	1. ,109.,0
0	7	12	42	1. ,109.,0
0	0	26	00	0. ,1.0 ,0
3	0	26	0	0. ,1. ,0
4	0	26	0	0. ,1. ,0
0	0	32	0	.5 ,115.,0
0	0	34	80	.15,180.,0
0	0	34	0	.5 ,109.,0
0	0	62	80	.15,180.,0
0	2	37	80	.5 ,120.,0
3	2	37	80	.5 ,60. ,0
4	2	37	80	.5 ,85. ,0
0	2	38	80	.5 ,120.,0
0	3	38	80	.5 ,85. ,0
3	3	38	80	.5,120. ,0
4	3	38	80	.5, 60. ,0
0	0	61	0	.45,120.,0
0	20	46	62	.4 ,180.,0
0	20	46	63	.4 ,180.,0
0	46	63	80	.50,180.,0
3	80	61	80	.25,120.,0
0	-1	61	0	.8 ,0 ,0
3	22	61	80	.25,120.,0

---

rectly typed according to the model. All *cp* and *cp\** atoms were converted to type 40 aromatic carbon as were all phenyl group carbons to avoid  $\pi$  calculations. In particular, it should be noted that bonds to carbonyls and carbynes were both originally modeled with a type 4 carbon as are the acetylides and isocyanides. When bond orders were incorrectly generated from the distance criteria within PCModel, they were changed appropriately. Although MMX has the capability of coordinating ligands to a metal via the lone pairs of electrons on the atom, this was avoided completely.

#### BONDLEN PROGRAM

BONDLEN was written to search through collected sets of structural data from user-determined bonding and atoms patterns and to produce statistical output of metal-ligand bond distances based on these data. A bonding pattern could be specified by a set of simple descriptive commands, and

the minimized or experimental structural data could be searched for that bonding pattern. The pattern description includes atom type, metal type, and metal coordination type.

#### BONDANG PROGRAMS

BONDANG was written to search through collected sets of structural data from user-determined bonding and atoms patterns and to produce statistical output of ligand-metal-ligand angles and metal-ligand-ligand angles based on these data. Like BONDLEN, the ligand atom types, metal type, and metal coordination can be specified by a set of simple descriptive commands, and the minimized or experimental structural data could be searched for that pattern.

#### PARAMETER OPTIMIZATION BY SIMPLEX

In an effort to improve the fit of experimental and calculated bond lengths a Simplex optimization was performed where the response function

**TABLE IV.**  
**Covalent Radii Current Model.**

Metal	Radius
Li	1.510
Na	1.85
K	2.30
Rb	2.44
Be	0.0
Mg	1.60
Ca	2.00
Sr	2.15
Sc	1.60
Y	1.85
La	1.85
Ti	1.481
Zr	1.56
Hf	1.60
V	1.355
Nb	1.455
Ta	1.455
Cr	1.30
Mo	1.423
W	1.431
Mn	1.253
Tc	1.22
Re	1.355
Fe	1.222
Ru	1.357
Os	1.355
Co	1.26
Rh	1.355
Ir	1.22
Ni	1.25
Pd	1.40
Pt	1.40
Cu	1.13
Ag	1.35
Au	1.25
Zn	1.309
Cd	1.51
Hg	1.51

was the sum of the squares of all bonds between the metal and its directly bonded, not coordinated, ligands, and the parameters to be fit were all of the atom covalent radii and the standard metal ligand bond distance whose dependence was only on the ligand. The values were then tuned by visual inspection to give the current model.

### Model Performance

1. *Bond Distances.* With the original model the overall mean deviation between calculated

and experimental distances is 0.022 Å, but with a standard deviation of 0.178 Å. Thus, although reasonable structures are generally obtained, the deviations are large. Nonetheless, some of the successes of the original model include the treatment of metal carbonyls with a mean and standard deviation of 0.006 and 0.064 Å, respectively. Phosphine ligands on chromium, molybdenum, and ruthenium are well treated, but those on cobalt and on the nickel triad are calculated to be 0.1–0.15 Å longer than experimental values.

The current model with the metal–ligand bond distances of Table III and the metal radii of Table IV does much better than the original model with the CSD data set. Table V gives a summary of the average and standard deviations for the metal–ligand bond distances using the parameters of Tables III and IV.

2. *Bond angles.* In the original model, the bond angles in octahedral complexes are generally reproduced reasonably well. For carbonyl–carbonyl angles between 80° and 110° the mean deviation between experimental and calculated values is  $-0.61^\circ$ , with a standard deviation of  $4.28^\circ$ . With phosphine–phosphine angles in this range, the mean deviation is  $2.54^\circ$ .

In the current model, bond angles are also reasonably calculated. See Table VI for a summary of average and standard deviations of the more common angles encountered in the data set.

## Discussion

Recognizing the variety of bonding patterns and oxidation states in transition metal complexes, the object in developing the current force field was to provide a general steric model at the metals for these systems that would also include ligand–metal–ligand Coulombic terms, yet retain the MM2-like force field for the ligand. Thus, it was important to disregard 1,3- bond angle and 1,4-torsions involving the metal and include only distances and force constants for the metal–ligand bond. It was important to ignore the oxidation state in the description of these parameters, but,

TABLE V.  
Statistical Data for Metal–Ligand Distances Using the Current Model.

Ligand atom type	Metal with average deviation, standard deviation (Å), and number of occurrences below											Ave. dev. Std. dev. #
	Co	Cr	Fe	Mo	Ni	Pd	Pt	Ru	Ti	W	Zr	
1	0.009	0.012	0.000	−0.001	0.007	−0.018	0.000	0.000	−0.029	0.000	−0.041	
	0.017	0.024	0.000	0.033	0.037	0.018	0.000	0.000	0.030	0.000	0.041	
	47	12	0	8	19	1	0	0	16	0	1	
2	0.012	−0.016	0.028	0.027	−0.022	0.000	0.000	0.043	−0.011	0.000	0.000	
	0.018	0.020	0.028	0.040	0.048	0.000	0.000	0.043	0.027	0.000	0.000	
	16	9	6	3	8	0	0	8	11	0	0	
3	−0.010	0.040	0.009	0.002	−0.017	0.000	−0.037	−0.057	−0.035	0.000	0.000	
	0.010	0.040	0.018	0.002	0.036	0.000	0.037	0.067	0.035	0.000	0.000	
	1	2	3	1	6	0	1	3	1	0	0	
4	0.006	0.014	0.000	0.011	0.012	0.000	0.000	0.000	0.000	0.000	0.000	
	0.014	0.014	0.000	0.011	0.013	0.000	0.000	0.000	0.000	0.000	0.000	
	5	23	0	26	10	0	0	0	0	0	0	
5	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.030	0.000	0.000	0.000	
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.030	0.000	0.000	0.000	
	0	0	0	0	0	0	0	2	0	0	0	
6	0.010	0.039	0.000	0.023	0.026	0.000	0.000	0.000	−0.016	0.000	0.000	
	0.016	0.052	0.000	0.023	0.026	0.000	0.000	0.000	0.016	0.000	0.000	
	12	4	0	1	7	0	0	0	1	0	0	
7	0.000	0.000	0.000	0.021	−0.002	0.000	0.000	0.000	0.000	0.000	0.000	
	0.000	0.000	0.000	0.042	0.002	0.000	0.000	0.000	0.000	0.000	0.000	
	0	0	0	2	2	0	0	0	0	0	0	
8	0.010	−0.015	0.000	0.020	−0.004	0.000	0.000	0.000	−0.024	0.000	0.000	
	0.010	0.015	0.000	0.020	0.009	0.000	0.000	0.000	0.024	0.000	0.000	
	8	3	0	2	7	0	0	0	1	0	0	
9	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
	0.010	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
	147	0	0	0	0	0	0	0	0	0	0	
10	0.000	0.037	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
	0.000	0.037	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
	0	1	0	0	0	0	0	0	0	0	0	
11	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
	0	0	0	0	0	0	0	0	0	0	0	
12	0.000	−0.004	0.000	0.000	−0.086	0.000	0.000	0.000	−0.039	0.010	−0.139	
	0.000	0.022	0.000	0.000	0.086	0.000	0.000	0.000	0.040	0.010	0.139	
	0	3	0	0	8	0	0	0	8	1	1	
13	0.000	0.022	0.000	−0.017	−0.028	0.000	0.000	0.000	0.000	0.000	0.000	
	0.000	0.022	0.000	0.024	0.028	0.000	0.000	0.000	0.000	0.000	0.000	
	0	6	0	2	3	0	0	0	0	0	0	
14	−0.033	0.025	0.000	−0.015	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
	0.033	0.025	0.000	0.016	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
	2	1	0	3	0	0	0	0	0	0	0	
15	−0.052	0.007	0.000	0.007	−0.013	0.000	0.000	0.000	0.000	0.000	0.000	
	0.052	0.021	0.000	0.018	0.013	0.000	0.000	0.000	0.000	0.000	0.000	
	2	2	0	9	1	0	0	0	0	0	0	
19	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
	0	0	0	0	0	0	0	0	0	0	0	
22	0.027	0.032	0.000	0.022	−0.006	0.000	0.001	0.000	0.000	0.000	0.000	
	0.027	0.032	0.000	0.023	0.017	0.000	0.001	0.000	0.000	0.000	0.000	
	3	1	0	5	3	0	1	0	0	0	0	



TABLE V.  
(Continued)

Ligand atom type	Metal with average deviation, standard deviation (Å), and number of occurrences below										
	Co	Cr	Fe	Mo	Ni	Pd	Pt	Ru	Ti	W	Zr
25	−0.009	0.020	0.000	0.010	−0.013	−0.024	−0.020	0.026	−0.013	0.000	0.000
	0.013	0.020	0.000	0.011	0.023	0.024	0.020	0.026	0.045	0.000	0.000
	25	10	0	8	51	1	2	1	4	0	0
37	−0.008	0.002	0.000	0.048	0.013	−0.004	0.000	0.000	−0.017	0.000	0.000
	0.015	0.004	0.000	0.048	0.013	0.004	0.000	0.000	0.017	0.000	0.000
	39	13	0	4	6	3	0	0	1	0	0
40	−0.018	0.015	0.020	0.000	−0.004	0.009	0.000	0.000	−0.016	0.000	0.000
	0.027	0.015	0.020	0.000	0.026	0.009	0.000	0.000	0.016	0.000	0.000
	4	14	2	0	14	1	0	0	8	0	0
41	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0	0	0	0	0	0	0	0	0	0	0
61	0.005	0.027	0.000	0.026	−0.034	0.000	0.000	0.000	0.007	0.021	0.000
	0.023	0.027	0.000	0.026	0.034	0.000	0.000	0.000	0.007	0.021	0.000
	2	28	0	4	1	0	0	0	1	7	0
62	0.000	−0.003	0.000	−0.059	0.000	0.000	0.000	0.000	0.000	−0.023	0.000
	0.000	0.021	0.000	0.059	0.000	0.000	0.000	0.000	0.000	0.023	0.000
	0	5	0	1	0	0	0	0	0	2	0
63	−0.008	0.010	−0.025	0.006	−0.013	0.000	0.000	−0.014	−0.004	0.009	0.000
	0.009	0.012	0.026	0.009	0.036	0.000	0.000	0.016	0.004	0.009	0.000
	31	158	31	40	6	0	0	30	1	22	0
pi40	−0.032	−0.041	−0.014	−0.008	0.020	0.000	0.000	0.034	0.032	0.032	−0.017
	0.067	0.052	0.017	0.069	0.026	0.000	0.000	0.034	0.062	0.045	0.032
	60	23	45	110	77	0	0	10	215	35	10

TABLE VI.  
Ligand–Metal–Ligand Bond Angles Using the Current Model.

Types	Metal types with average and standard deviations and number of occurrences										
	Co	Cr	Fe	Mo	Ni	Pd	Pt	Ru	Ti	W	Zr
1 25	0.3	−0.1	0.0	0.0	2.2	0.0	0.0	0.0	0.0	0.0	0.0
	0.4	0.1	0.0	0.0	2.5	0.0	0.0	0.0	0.0	0.0	0.0
	10	2	0	0	6	0	0	0	0	0	0
1 63	−2.1	0.0	0.0	0.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	2.1	0.0	0.0	1.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	2	0	0	3	0	0	0	0	0	0	0
2 25	−5.0	0.0	0.0	0.0	−0.1	0.0	0.0	0.0	0.0	0.0	0.0
	5.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0
	2	0	0	0	2	0	0	0	0	0	0
2 63	0.0	0.0	−2.6	0.0	0.0	0.0	0.0	0.0	−1.2	0.0	0.0
	0.0	0.0	2.6	0.0	0.0	0.0	0.0	0.0	1.2	0.0	0.0
	0	0	7	0	0	0	0	0	2	0	0
3 25	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0	0	0	0	0	0	0	0	0	0	0
3 63	0.4	0.6	0.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0.4	0.6	2.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	1	6	9	0	0	0	0	0	0	0	0

TABLE VI.  
(Continued)

Metal types with average and standard deviations and numbers of occurrences											
Types	Co	Cr	Fe	Mo	Ni	Pd	Pt	Ru	Ti	W	Zr
13 25	0.0	−0.3	0.0	0.8	0.7	0.0	0.0	0.0	0.0	0.0	0.0
	0.0	0.4	0.0	0.8	0.7	0.0	0.0	0.0	0.0	0.0	0.0
	0	3	0	2	4	0	0	0	0	0	0
13 63	0.0	0.1	0.0	−1.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0.0	0.4	0.0	1.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0	19	0	2	0	0	0	0	0	0	0
14 25	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0	0	0	0	0	0	0	0	0	0	0
14 63	0.0	0.0	0.0	3.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0.0	0.0	0.0	3.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0	4	0	4	0	0	0	0	0	0	0
22 25	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0
	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0
	0	0	0	0	2	0	0	0	0	0	0
15 25	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0.0	0.0	0.0	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0	0	0	2	0	0	0	0	0	0	0
15 63	0.0	0.6	0.0	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0.0	0.7	0.0	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0	7	0	1	0	0	0	0	0	0	0
22 63	0.8	0.0	0.0	1.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	5.3	0.0	0.0	2.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	6	0	0	3	0	0	0	0	0	0	0
25 25	−0.3	0.0	0.0	1.0	0.6	0.0	0.3	0.0	2.8	0.0	0.0
	0.4	0.1	0.0	1.1	1.1	0.0	0.3	0.0	2.8	0.0	0.0
	2	7	0	4	23	0	1	0	2	0	0
25 40	−1.1	0.0	0.0	−1.7	−1.1	0.0	0.0	0.0	−1.6	0.0	0.0
	1.1	0.0	0.0	1.7	1.1	0.0	0.0	0.0	1.6	0.0	0.0
	23	0	0	10	27	0	0	0	14	0	0
25 61	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0	0	0	0	0	0	0	0	0	0	0
25 63	1.6	−0.3	0.0	−0.1	0.0	−2.5	0.0	1.0	0.0	0.0	0.0
	1.6	0.8	0.0	0.6	0.0	2.5	0.0	1.0	0.0	0.0	0.0
	5	8	0	2	0	2	0	3	0	0	0
61 63	0.0	−0.5	0.0	−0.9	0.0	0.0	0.0	0.0	0.0	1.2	0.0
	0.0	0.6	0.0	0.9	0.0	0.0	0.0	0.0	0.0	2.2	0.0
	0	35	0	2	0	0	0	0	0	8	0
62 63	0.0	−0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0.0	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0	2	0	0	0	0	0	0	0	0	0
63 63	1.9	0.4	2.7	2.7	8.2	0.0	0.0	4.6	0.0	1.5	0.0
	2.6	0.6	3.7	3.0	8.5	0.0	0.0	5.0	0.0	3.1	0.0
	32	273	34	33	6	0	0	30	0	23	0
Metal—P—O											
25 0	0.6	−0.2	0.0	−0.3	0.0	0.5	0.7	−0.8	−0.2	0.0	0.0
	0.8	0.4	0.0	0.7	0.9	1.2	1.0	0.8	1.8	0.0	0.0
	75	30	0	24	153	3	6	3	12	0	0
Metal—CO											
63 46	−0.3	0.0	−0.9	−0.3	0.6	0.0	0.0	−1.1	0.2	−0.4	0.0
	1.0	1.1	1.1	1.4	2.2	0.0	0.0	1.4	0.2	1.2	0.0
	31	162	31	42	6	0	0	30	1	22	0

subsequently, deviations from the 18-electron rule resulted in structural changes that had to be considered by the force field. The original formulation reproduced many of the coordinately saturated structures in ref. 4, such as the metallocenes and carbonyl compounds.

The original and current formulations of the force field increase the covalent radius of the metal by 0.15 Å when the total electron count at the metal exceeds 18, and this seems to describe appropriately the small number of compounds in the database that can be evaluated in this manner, although cobaltocene distances calculated are too long by ca. 0.13 Å. However, nickelocene, which contains a 20-electron metal, has distances calculated to be only 0.06 Å too long with the correction used.

The original and current formulations treat coordinately unsaturated metallic systems, by simply increasing the covalent radius of the metal by 0.15 Å when it is involved in coordination with a  $\pi$

system. Although this appears to be a good average, 17-electron systems like ferricenium cation have Fe—C distances only 0.06 Å longer than ferrocene itself.<sup>4</sup> Perhaps, subsequent formulations of this force field might take into account the degree of unsaturation in making corrections.

It is remarkable that such a simple mechanical model as presented here provides such a reasonable fit to so much data. Clearly, the model cannot distinguish between tetrahedral and square-planar complexes, but, if told which, the reproduction in distances is good.<sup>7</sup> The current model, therefore, is proposed as a standard by which specific interactions in real molecules might be judged. If deviations in distances, angles, or torsion are in evidence, then specific electronic interactions should perhaps be pursued.

## Appendix

**TABLE A-I.** Compounds from the Cambridge Crystallographic Database Used for Evaluation.

acbcra10	boyjuu00	chvicr00	cukzox00	mpfpni00
acbcrb10	boysaj00	cihnow00	culkid00	mphcpt01
accpti00	boysen00	cilgaf00	cummus00	msmpcr10
actpen00	boyzoe00	cipcuz00	czbacr00	mstfni00
alcpmo00	bpcpcr00	cipdag00	deapcc00	mynbco00
bacrun00	btbicr00	cirmiz00	dipnip00	nealti00
bacrun10	btclay00	cizlay00	dmdeco01	nicbfe00
bahciw00	bubsas00	cmcpco00	dpbpcr00	ninprmy00
balvit00	bubsew00	cmphcr00	dtynecr10	pabpcr00
bamcoh00	budyuu00	cmpiti00	eacbcrr00	pbzmmi00
batmue00	bujfiv00	cobalx10	eaivco00	peacni10
baygaj00	bulwek00	cobdec00	ealpcr10	peamcr10
bayxaa00	bumbam00	coccus00	ecosar00	peamni00
bcmpcr00	butgec00	cocdaz00	emaccr00	peepni00
bcnmob00	butmoa10	cocrw00	epebni00	peepni01
bcpbcb00	butxod00	cofwaj00	febzco10	pemgic10
bebtux00	buxxat00	cofwup00	fertit00	pesicr00
bebtux10	buxxex00	cogpap00	fmpfco00	pfpbti00
befyam00	buznit00	cojbos00	fmsicr00	pgecbcr00
begxoar00	bzocxo00	cojsav00	fpcnic00	phcbcr00
begxug00	cacvil00	cojsez00	hfacni10	phcfpn10
betdaf10	cahfas00	comoni10	hglico10	picycr00
betdej10	cajsip00	conbiq00	hpetni00	pmenpn00
bevwi00	cajwoz00	corhog00	hxpman00	pmhpy00
bexxor00	calsir00	corhum00	ipalcr00	pmphcr00
bexxux00	camver00	cormax00	ippmni10	pnihep00
beydak00	capjei00	cormeb00	itonco00	pscomp10
bibkec00	cascuu00	cosxaj00	mamnip00	psibti00
bicaen10	catpoc00	cotwen00	mapcti00	pysini00
bidmuw00	catpui00	cozyar00	mbagco00	raccyc10
bijhux00	catyif00	cpcbcr00	mcbccr00	raccyc11
bikini00	catyol00	cpfmni00	meamcr10	sncocr00

**TABLE A-I.**  
(Continued)

bildij00	cavfua00	cpfpco00	mebgco00	sphenc00
bilwic00	cavgah00	cpfpni10	mebgco01	sscebc00
binniv10	cbabmo10	cpnife00	mebgco02	sscebc01
binnob10	cboxmb10	cpnife10	meglco00	tbcbfe00
bipnod00	cbpati00	cppmxt00	mglcoa00	thftcc10
bipzdn00	cecvel00	cpppni10	mglcoa01	thylcr10
birlix00	cecezp00	cpticb00	mglpco00	tmsicr00
bivfiv00	cedsaf00	cptpti00	mgxpcq00	topfco10
bivfob00	cedsej00	csinia00	mncpti00	tpfeco00
bixfuj00	cegyao00	csinib00	mopcrb10	txtcni00
bmpfpn00	cesgai00	cugpav00	mpcomp00	vhtdco00
bodrer00	cesgail0	cuklez00	mpcmpt10	wtcxcr00
bolcio00	cesncc00	cukloj00	mpeycr00	wtcxcr10
boybia00	ceycoy00	cuklup00	mpeycr10	zeggib00

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- Serena Software, Box 3076, Bloomington, IN 47402. The parameters are available on the web at [www.serenasoft.com](http://www.serenasoft.com).
- The original version of this study included three structures, **badhod00**, **cedmed00**, and **cijkov00**, which gave substantial deviations in OC—M—CO bond angles (but not distances) for reasons that are not obvious. They were removed from the data set.